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A review on development of industrial processes and emerging techniques for production of hydrogen from renewable and sustainable sources

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ABSTRACT

Hydrogen is considered as the fuel for next generation and extensive research is being pursued for search of new techniques for hydrogen production from renewable sources. There is a diverse collection of hydrogen production processes at their different stages of development. This review paper analyzes the industrial and emerging hydrogen production technologies. These processes include steam methane reformation, partial oxidation, autothermal reforming, steam iron, plasma reforming, thermochemical water splitting and biological processes. Till date, steam reformation of methane is the most used industrial technique and its efficiency can go up to 85%. It meets up to 50% of total hydrogen consumption in the world. Continuous research is going on to enhance production yield as well as to improve the process economics. Considerable work is going on about sorption enhanced reforming and membrane reactor for this purpose. Partial oxidation and autothermal reforming processes are the other two processes which are also used for industrial. The most sought process is the thermochemical water splitting using sunlight. Several research institutes are engaged in the development of hydrogen production technologies using renewable sources. Plasma reformation and biological processes are intensively worked out throughout the globe. The present article reviews the recent developments in industrial techniques which will lead to enhancement of hydrogen production. The non-conventional techniques are described in this article as emerging techniques, which are the promising approaches for hydrogen production from biomass, an abundant, clean and renewable source.

Contents

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1. Introduction

Hydrogen is considered the most promising and important fuel for the future as it has tremendous capability of reducing environmental pollution. Hence, there is ever increasing interest worldwide in order to minimize the greenhouse effect and other environmental pollutant gases. It is considered that vehicles operating on hydrogen can dramatically reduce dependence on fossil fuel and significantly reduce tailpipe emissions. Thus, the use of hydrogen as fuel unlocks potential means of storing and delivering energy from abundant, domestically available resources—while reducing carbon footprint [1]. It is envisaged that fuel application of hydrogen will enjoy a smooth entry into the automotive industry as fuel cell cars and it would be three times as energy efficient as internal combustion engine cars of comparable performance without emitting air pollutants [2].

It is observed that there have been transitions from solid to liquid to gaseous fuels as major energy sources. There are demands for decarbonization of energy sources [3] due to environmental concerns. Huge amount of funding is provided for research on the production, distribution, storage and use of H_2, especially in countries such as the United States, the European Union and Japan [4–6]. The advantages of using hydrogen are abundant availability, utilization of a variety of feedstocks and a variety of production technologies [7]. However, some critics doubt whether H_2 is the right solution for the energy-related environmental, security and sustainability issues or not. They argue that the current technology for producing H_2 as an energy carrier is too costly and wasteful of energy [8]. According to Romm [9] there are two important pillars upon which the H_2 economy rests: pollution-free sources for the H_2-generation and fuel cells for converting H_2 to useful energy efficiently. Global consumption of hydrogen in different sectors is shown in Fig. 1 [10].

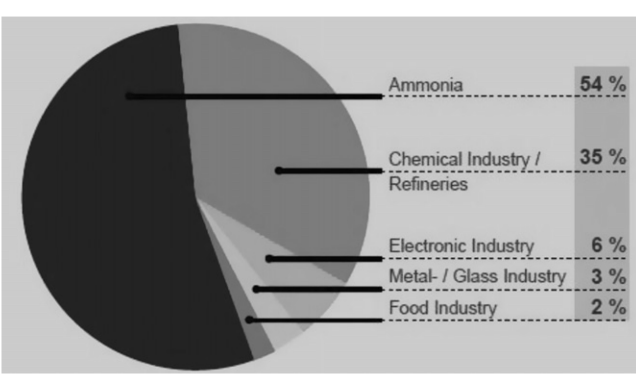


Fig. 1. Hydrogen consumers in the world [10].

The increasing global energy demand speeds up the depletion of fossil fuel resources which adds to the motivation for search for alternative resources. In addition, there is an increasing demand for hydrogen with major applications in refinery use and as a component in synthesis gas for the manufacture of methanol and ammonia. Currently it is also anticipated that renewed interest in Fisher–Tropsch technology [GTL (gas-to-liquid)/CTL (coal-to-liquid)/BTL (biomass-to-liquid)] will further enhance the demand of hydrogen. Hence, it is imperative to expand current hydrogen production capacity in order to meet the increasing hydrogen demand [11]. Government and private entrepreneurs can work together to expedite the progress in improving the efficiency and economics of hydrogen production [2]. In this review article, we present a survey of existing industrial and emerging processes used for hydrogen production.

2. Classification of hydrogen production methods

Due to the highly reactive nature of hydrogen, it does not exist in free state in nature, but is always found in combined state with other elements. Hydrogen is abundantly available in natural sources like hydrocarbon, water and biomass [4] which are the major feedstock for hydrogen production (Fig. 2) [12]. Extraction/production of hydrogen involves chemical processing and energy input. Based upon the nature of chemical process and/or energy input, hydrogen production methods are broadly classified into three major categories: thermochemical, electrochemical and biological methods. In the following sections, the methods of hydrogen production and their industrial application are briefly described.

2.1. Thermochemical methods

The thermochemical methods consist of chemical reactions for the separation of hydrogen from its feedstock which are driven by thermal energy inputs either externally or internally generated and the reactions are either oxidative or non-oxidative.

2.1.1. Oxidative process

This process involves the degradation of feedstock at high temperature (> 700 °C) in the presence of oxidants such as oxygen/air, steam, CO_2 or a combination of two or more oxidants. The oxidative conversion of hydrocarbons to hydrogen can be represented by the following general chemical equation:

$$C_nH_m+[O_x]\rightarrow xH_2+yCO+zCO_2 \quad (1)$$

where C_nH_m is a hydrocarbon ($n\geq1$, $m\geq n$) and $[O_x]$ is an oxidant such as O_2, H_2O and CO_2. The oxidative process for hydrogen production includes well established industrial technologies such

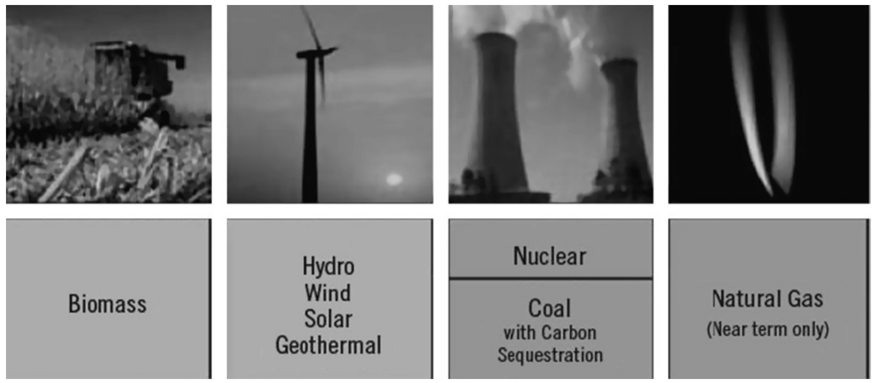


Fig. 2. Sources of hydrogen [12].

as steam methane reformation (SMR), partial oxidation (PO_x), autothermal reforming (ATR), steam-iron process (SIP), and CO_2 reforming of methane.

2.1.2. Non-oxidative process

Here, the degradation of feedstock involves the direct splitting of C–H bond under the influence of different sources of energy like heat, plasma, radiation etc. The chemical equation which describes this process is given as follows:

$$C_nH_m+[E]\rightarrow xH_2+yC+zC_pH_q \tag{2}$$

where C_nH_m is the hydrocarbon feedstock ($n\geq1$, $m\geq n$), C_pH_q represents relatively stable products of the feedstock cracking ($z\geq0$, $p\geq1$, $q\geq p$; in most cases C_pH_q is CH_4 or C_2H_2) and $[E]$ is an energy input [13].

2.2. Electrochemical methods

This method is accompanied by the passage of an electric current and resulted in the occurrence of chemical reaction along with the liberation or absorption of heat. It is divided into two categories depending upon the source of energy input.

(i) Electrolysis: it involves the breakage of water molecules into hydrogen and oxygen by passing electricity between two electrodes, resulting in chemical reactions at the electrodes and separation of materials. This may be the cleanest technology but this method costs around 80% of the operating cost of hydrogen production and is very expensive [14].
(ii) Photoelectrochemical: in this process energy is derived from photons. This is briefly explained in the section of Emerging Techniques (Section 4).

2.3. Biological methods

Hydrogen is produced from renewable sources either biologically or photo-biologically by the anaerobic and photosynthetic microorganisms using carbohydrate-rich and non-toxic raw materials. Under anaerobic conditions, hydrogen is produced as a by-product during conversion of organic wastes into organic acids, which are then used for methane generation. Acidogenic phase of anaerobic digestion of wastes can be manipulated to improve hydrogen production. Photosynthetic processes include algae, which use CO_2 and H_2O for hydrogen gas production. Some photo-heterotrophic bacteria utilize organic acids such as acetic, lactic and butyric acids to produce H_2 and CO_2 [15,16]. A successful biological conversion of biomass to hydrogen depends strongly on the processing of raw materials to produce feedstock, which can be fermented by the microorganisms [17]. The biological method is considered as a promising way of producing hydrogen as it provides a feasible means for a sustainable supply of H_2 with low pollution and high efficiency [18]. This is briefly explained in the section of Emerging Techniques (Section 4).

3. Industrial processes

In this section, we review the established industrial hydrogen production methods. Table 1 [19] presents a list of hydrogen production techniques. Out of the 22 mentioned techniques, only few are considered as an industrial process for hydrogen production which are given as follows:

(i) steam methane reformation
(ii) partial oxidation
(iii) auto-thermal reformation
(iv) steam-iron process.

There are a number of feedstocks from which hydrogen is produced industrially but the most favored feedstock is natural gas due to its abundant availability and advantageous price [20]. Apart from natural gas, light alcohols like methanol and ethanol are used as these can be handled easily and are widely distributed over the globe [21–23]. In particular, ethanol has been utilized as a promising source because of its low toxicity, high volumetric energy density and its availability [24,25].

3.1. Steam methane reformation (SMR)

SMR is commercially proven, cost effective technology with gaseous and liquid hydrocarbon as its main feedstock. It has contributed to about 40–50% [26–28] of total hydrogen production. Pretreatment of the raw feed, reforming to synthesis gas, conversion to a hydrogen-rich gas, and purification to hydrogen are the basic steps of this process. The process typically occurs at temperatures of 800–1000 °C and pressures of 13–20 bar [29].

The basic chemical reactions for SMR are described by the following equations:

$$C_nH_m+nH_2O\rightarrow nCO+\left(n+\frac{m}{2}\right)H_2 \quad \Delta H<0 \tag{3}$$

$$CH_4+H_2O\leftrightarrow CO+3H_2 \quad \Delta H=-206\ \text{kJ/mol at } 15\ ^\circ C \tag{4}$$

$$CO+H_2O\leftrightarrow CO+H_2 \quad \Delta H=+41.2\ \text{kJ/mol at } 15\ ^\circ C \tag{5}$$

The higher efficiency in SMR is achieved by recycling and pressure swing adsorption purge gas can be burned as a fuel for a reformer burner to make steam to drive the endothermic

Table 1
Different methods of hydrogen production (based on www.hydrogenassociation.org and [19]).

Primary Method	Process	Feedstock	Technique
Thermochemical	Oxidative	Liquid and gaseous hydrocarbon	Steam methane reforming
			Autothermal reforming
			Partial oxidation
			Combined reforming
			Steam-iron process
			CO_2 reforming of methane
			Plasma reforming
			Photocatalytic conversion
		Coal	Gasification
		Biomass	Pyrolysis
			Gasification
	Non-oxidative	Liquid and gaseous hydrocarbon	Thermal decomposition
			Catalytic decomposition
			Refinery processes
			Plasma
		Biomass	Pyrolysis
		Water	Thermochemical water splitting
Electrochemical	Electrolysis	Water	Electricity
	Photoelectrochemical	Water	Direct sunlight
Biological	Photobiological	Water and algae	Direct sunlight
	Anaerobic digestion	Biomass	High temperature heat
	Fermentative microorganism	Biomass	High temperature heat

reaction for SMR [30]. The reforming of fossil fuel is a mature technology which uses existing fuel infrastructures and reduces the need for transport and storage of hydrogen. Hence, extensive research work is being carried out on steam reforming of methane [31,32], methanol [33,34] and ethanol [35].

SMR is a major industrial process for H_2 production and the catalyst plays a vital role in the SMR process. The development of an efficient steam reforming catalyst is a very active area of research [13]. In order to obtain acceptable reaction rates, a catalyst is required to accelerate the process [36]. Due to the involvement of high temperatures and pressures in the SMR process, catalysts must be formulated carefully and shaped to ensure desired performance [37]. Noble metals (Ru, Rh, Ir, Ni, Pt, and Pd) and nickel are considered as the best catalysts for the SMR process [38].

However, disadvantages are usually associated with the reformers which are complex, large and expensive and have relatively long warm-up time and can introduce additional losses into the energy conversion process. In most industrial applications, hydrogen is required at a pressure of around 20 bar, therefore, the reformers are operated at elevated pressures (usually, 20–26 bar). High pressures allow for a more compact reactor design, thus increasing the reactor throughput and reducing the cost of materials. To supply heat for the endothermic SMR reaction, the catalyst is loaded into a bundle of reactor tubes (about 15 m long and 12 cm inside diameter) made out of heat-resistant Ni alloy [13,39].

As SMR involves a multi-step process with severe reaction conditions, there is enough scope for improvement regarding energy efficiency, gas separation and H_2 purification techniques. Sorption enhanced reforming, membrane reactors and hybrid adsorbent-membrane reactors are introduced in SMR for enhanced H_2 production.

3.1.1. Sorption enhanced reforming (SER)

SER is used in the form of a fixed packed column of an admixture of SMR catalyst and a chemisorbent to remove CO_2 selectively from the reaction zone. In the SER process SMR, WGS (water gas shift) and CO_2 removal steps occur simultaneously in the presence of a nickel-based catalyst and a calcium-based sorbent. This process consists of four steps: initially the reactor

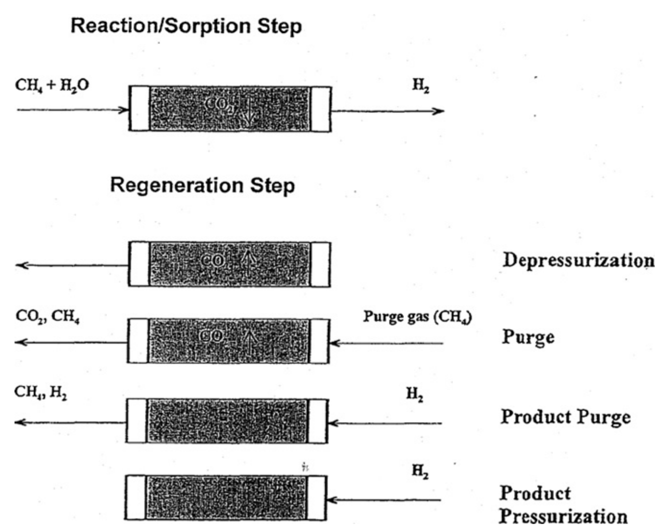


Fig. 3. Example of H_2-SER process steps [29].

is pre-saturated with a mixture of steam and H_2 at a desired reaction temperature and pressure. Steam and methane at a prescribed ratio are fed to the reactor and an enriched H_2 product is collected as the reactor effluent. This reaction step is continued until the H_2 purity in the product decreases to a preset level. Then the feed is diverted to the second identical reactor where it is counter-currently depressurized. The effluent gas can be recycled as feed to another reactor or used as a fuel. In the third step, the reactor is counter-currently purged with a mixture of 5–10% H_2 in steam to desorb CO_2; here the desorbed gas contains CH_4, CO_2, H_2 and H_2O. The desorbtion pressure may range between 0.2 and 1.1 bar. The last step is the pressurization step in which the reactor is counter-currently pressurized to the reaction temperature with the steam/H_2 mixture. The regeneration of the reactor is complete and it is ready to undergo a new cycle as shown in Fig. 3 [29].

The CO_2 formed is adsorbed by an adsorbent which, once saturated with CO_2, is regenerated in situ via the principles of pressure swing adsorption or commonly by using steam. The amount of steam required for the removal of adsorbed CO_2 from the saturated sorbent ascertains the efficiency of the system and the process. The process is therefore cyclic and each reactor

must undergo repetitive reaction/regeneration steps and a continuous hydrogen-rich product can be obtained from the system [29,40–42]. The potential benefits of using the SER method as compared with conventional SMR are low temperature (400–500 °C) requirement, production of hydrogen at feed gas pressure of 1–4 bar, reduction of purification steps, minimization of side reactions and reduction of excess steam used in conventional SMR. This process is capable of producing high-purity hydrogen containing minimal carbon monoxide in a single processing step and also has the potential for producing pure CO_2 that is suitable for subsequent use or sequestration during the sorbent regeneration step [42,43]. The comparison between operating characteristics of SMR and SER is given in Table 2 [29].

The adsorbent plays an important role in SER and the adsorbent must have some properties like high selectivity and adsorption capacity at operating conditions, stable adsorption capacity of carbon dioxide after repeated adsorption/desorption cycles and adequate mechanical strength of adsorbent particles after cyclic exposure to high pressure streams [44–46]. Initially, K_2CO_3–hydrotalcite has been used as an adsorbent at a temperature of 450 °C instead of sorbent for removing CO_2 from the SMR reaction [47,48]. Harrison and Peng [43] have developed sorption-enhanced production of low-carbon monoxide hydrogen in their laboratory that has proved the feasibility of producing more than 95% hydrogen (dry basis). They have also described sorption-enhanced reaction conditions required to produce >95% hydrogen containing low carbon monoxide concentrations suitable for direct use in proton exchange membrane fuel cells. Yoon et al. [49] have shown that addition of calcium-based-carbon dioxide sorbents to the catalyst used in SMR increases the production of hydrogen to 92%+ in a combined process with carbonation and calcination and the cost of raw materials is cheaper than that of the K_2CO_3–hydrotalcite used in SER. Hydrotalcite is considered as a good CO_2 sorbent because it satiates the conditions like rapid kinetics, low cost, high CO_2 uptake and chemical stability at high H_2O concentration. The performance of different CO_2 sorbent materials is shown in Table 3 [40,41].

SER has high potential to reduce the production cost of hydrogen through lower capital and energy requirement [29]. The combination of reaction and separation in a single unit operation (such as adsorptive reactor, chromatographic reactor etc.) has an advantage for achieving enhanced conversions and yields in catalyzed reversible reactions [50–52]. A number of experiments have taken place to make the sorption process more competitive. Ida and Lin [53] have studied the effect of Li_2CO_3/K_2CO_3 dopant on lithium zirconate and have found that the CO_2 sorption rate increases due to the formation of a eutectic molten carbonate at high temperature. This molten carbonate can considerably reduce CO_2 diffusion resistance compared to the pure Li_2ZrO_3. Ochoa-Ferna´ndez et al. [54] have produced hydrogen with purity more than 95% and a concentration of carbon monoxide lower than 0.2 mol% using lithium zirconate as a sorbent and a hydrotalcite derived Ni catalyst as a steam reforming catalyst.

3.1.2. Membrane reactor

The membrane reactor is a device in which SMR, WGS and hydrogen purification steps take place in a single reactor. Methane and steam are fed into a catalyst filled reactor under pressure and Pd membrane is on one side of the reactor which is selectively permeable to hydrogen with high selectivity. As the steam reforming reaction proceeds, the hydrogen is driven across the membrane by the pressure difference. Depending on the temperature, pressure and the reactor length, methane can be completely converted and very pure hydrogen is produced and removed. This allows lowering of operation temperature and hence lowers material cost [30]. The scheme of pure hydrogen production in a membrane reactor is shown in Fig. 4 [55]. MRs can produce CO-free hydrogen without complicated H_2 purification units (e.g. CO catalytic converter, pressure swing adsorption (PSA)) and can exhibit high H_2 selectivity. This reactor results in more compact design and selective removal of hydrogen yields plus the conversion percentage is much better as compared to the conventional reactor [56,57]. One major advantage of this system is the simplified process design. A large number of industrial R&D activities have been reported on MRs [30]. Scientists and chemical engineers in the last few years have accomplished significant work in order to improve the MRs performances and to overcome problems like membrane durability, and resistance of the membrane

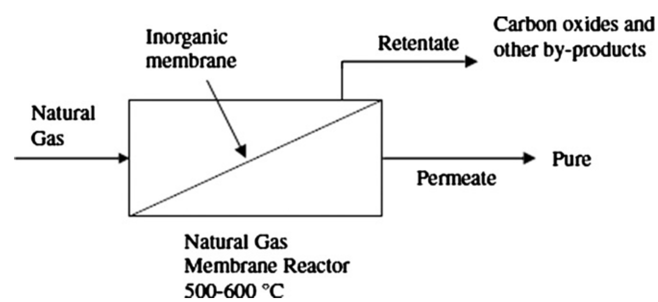


Fig. 4. Scheme of pure hydrogen production in a membrane reactor [55].

Table 2
Comparison between the operating characteristics of SMR and SER [29].

Sl. No.		Conventional SMR	SER goals
1.	Operating temperature	800–1000 °C	400–500 °C
2.	CH_4 to H_2 conversion	80–85%	90+%
3.	Reaction product composition (dry basis)	73.7% H_2+ 9.4% CO_2+ 12.0% CO+4.8% CH_4	98+% H_2
4.	Product pressure	14–28 bar	14–28 bar

Table 3
Characteristics of CO_2 sorbent materials [40,41].

Group	Representative member	Ads. cap.	Stability	Kinetics
1.Metal oxides	CaO	Good	Poor	Good
2.Hydrotalcites	$Mg_6Al_2(OH)_{16}[CO_3] \times 4H_2O/K_2CO_3$	Poor	Good	Poor
3.Double salts	$(K_2CO_3)(2KHCO_3)(MgCO_3)(MgO) \times xH_2O$	Fair	Unknown	Fair
4.Li metal oxides	Li_4SiO_4	Fair	Fair	Good
5.Supported sorbent	CaO on Cabot Superior micropowder [43]	Fair	Good	Good

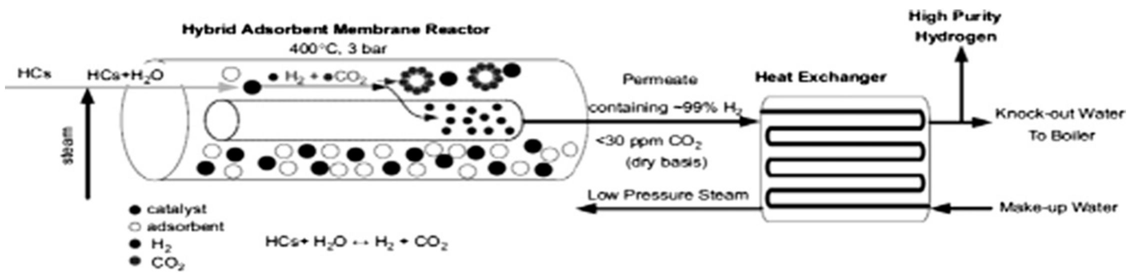


Fig. 5. The HAMR process for hydrogen production [81].

module seals to high temperature and pressure. The improvement in the MR technology brings them closer to the industrial utilization and their introduction in the industrial challenge strongly depends on the economics of the membrane process [58].

A number of experiments have been executed on the Pd based membrane in spite of its high cost. The Pd based membrane is considered as one of the promising membranes for hydrogen separation, because of its high stability at elevated temperature and extremely high hydrogen permselectivity based on the solution-diffusion transport mechanism [59]. Hoff et al. [60] have presented a good review on the modeling of membrane reactors. Delft et al. [61] have also identified Pd membrane as a promising option for hydrogen production in future power production systems and industrial chemical production processes after carrying out an R&D program on the development of Pd MR which focuses on thinner and cheaper palladium membranes with higher permeation rates, customized catalysts and the design of a feasible large scale membrane reformer. Basile et al. [62] have performed an experiment to investigate the behavior of the Pd/Ag membrane reactor in methanol conversion and have confirmed the good potential of the membrane reactor after achieving good methanol conversion at each temperature investigated and have carried out a number of experiments to compare the membrane reactor with fixed-bed reactor (FBR) [63] and conventional reactors [56,64] and found MR to be more efficient in respect of conversion efficiency, hydrogen yield and hydrogen selectivity. Yu et al. [65] have studied an ethanol reforming-catalytic membrane reactor with the WGS reaction (ECRW) in the permeate side to decipher the effect of sweeping gas flow rate on SMR, WGS reaction and concentration of the product. It is found that in ECRW-100 (100 ml/min), the high sweeping flow rate inhibited the SMR whereas in ECRW-70 (70 ml/min), the low sweeping flow rate facilitates the SMR and results in the improvement of hydrogen yield because of the catalytic activities of Pt/Degussa P25 (for WGS reaction) catalysts for SMR. On comparing ECRW-70 with a conventional reactor, the improvement in ethanol conversion and hydrogen recovery is found to be 11.9–19% and 78–87% respectively at a temperature range of 300–600 °C. Tosti et al. [66] have carried out an experiment to measure the hydrogen yield by varying operative parameters like temperature, pressure and membrane sweeping mode in a system consisting of traditional FBR and multi-tube Pd–Ag membrane reactor. The membrane module contained up to 19 Pd–Ag thin wall tubes which are capable of selectively separating the hydrogen produced. It is found that on feeding 500 g/h of water + ethanol (10.5:1) mixture, the membrane apparatus is able to produce more than 3.0–3.5 l/min of pure hydrogen whereas the hydrogen yield is observed to be close to 100% when operating at low feed flow rates of 200 g/h. They have also evaluated the ability of producing ultra pure hydrogen from Pd–Ag membrane reactor via oxidative steam reforming of ethanol (OSRE) under different operating conditions like temperature, pressure, feed molar ratio, and feed molar rate [67]. The Pd–Ag membrane reactor is filled with Pt-based catalyst and is characterized by complete hydrogen selectivity, high hydrogen permeability and good mechanical stability even after hydrogenation and thermal cycling. For evaluating hydrogen yield, the experiments have been performed at temperatures range of 400–450 °C and pressure of 1.5–2 bar; OSRE has been carried out by feeding membrane reactor with a gas stream containing a dilute water–ethanol mixture and air. They have tested different water/ethanol feed flow rates (5,10,15 g/h), several water/ethanol (4,10,13) and oxygen/ethanol (0.3,0.5,0.7) feed molar ratios and have found that the highest hydrogen yield of 4.1 moles per mole of ethanol fed is attained by using a $H_2/C_2H_5OH/O_2$ feed molar ratio of 10/1/0.5 at 450 °C and 2 bar.

3.1.3. Hybrid adsorbent-membrane reactor (HAMR)

The SER and MR show significant promise in the production of hydrogen but they are still not suitable or economic for small scale, on-site or on-board hydrogen production. The challenge in case of SER is to match the adsorbent properties with the catalytic system. Two typical types of adsorbents which are suggested for high temperature CO_2 removal are CaO and potassium promoted double layered hydrotalcite. CaO can operate effectively during SMR but requires a high temperature of 726 °C for regeneration. The regeneration condition is very harsh which may result in the deterioration of the adsorbent properties and sintering of the reforming catalyst. The mismatch between the reaction and the regeneration conditions makes the process more complicated [47,51,52,68–70]. Potassium promoted double layered hydrotalcite is shown to be a more effective CO_2 adsorbent and its regeneration temperature is low i.e. 200–450 °C [51,69]. MRs show significant importance in hydrogen production and utilize nanoporous inorganic or metallic Pd or Pd-alloy membranes. The Pd-alloy membranes are better suited for pure hydrogen production whereas metallic membranes are very expensive and become brittle during reactor operation or deactivate in the presence of sulfur or coke. Nanoporous membranes are better suited for SMR but they are difficult to manufacture without cracks and pin holes; as a result they often show inferior product yield. In addition, the hydrogen in the permeate side contains other gaseous products like CO_2, CO and CH_4 and further treatment is required for use in fuel-cell powered vehicles [71–74].

HAMR concept is originally proposed by Park et al. [75,76] which involves a hybrid pervaporation membrane reactor integrating reversible esterification and pervaporation steps through a membrane with water adsorption. Coupling reaction, pervaporation and adsorption significantly improve the performance of conventional membrane reactors (MR) and reduce temperature conditions. It is a combination of unique membrane and adsorption enhanced reactors and it is potentially more advantageous over MRs. HAMR couples the reaction and membrane separation steps together with adsorption. The HAMR is a cyclic process and it consists of four steps; in the first step the reactor is pre-saturated with H_2 and steam at the desired temperature and pressure. After that a mixture of steam:CO is fed into the reactor and the reaction is continued until the productivity specifications are met. When the H_2 purity and recovery decrease below the predetermined

levels, the feed is diverted to the second level. In the second step, the reactor is depressurized to atmospheric pressure counter-currently to the feed flow direction. The effluent stream during the blow-down step contains all components left in the reactor after step 1, and can be recycled as a feed to another reactor or used as a fuel. In the third step, the reactor is counter-currently purged with a weak adsorbing gas, in order to completely desorb CO_2 at atmospheric pressure. The desorbed gas mixture can again be recycled as a feed to another reactor or can be used as fuel gas. In the last step, the reactor is counter-currently pressurized to the reaction pressure with a mixture of steam and H_2. At this point, regeneration of the reactor is completed. In the four bed process, one bed consists of reaction-separation while the other three are involved in one of the regeneration steps [77].

Park [78] has also mathematically analyzed the HAMR system for hydrogen production undergoing SMR over a range of temperature and pressure and compared this with conventional packed-bed reactor and conventional MR. He has found that HAMR outperformed all the other conventional reactor systems; in HAMRF (with adsorption on the membrane feed-side) mode of operation, the methane conversion and hydrogen yield were nearly 100% and 98% respectively even under milder condition as compared to conventional reformer conditions. It is suggested that by introducing the CO_2 removal adsorbent system into the conventional MR, the chances of improvement of the performance of conventional methane-steam reformers as well as conventional MRs i.e. hydrogen production and reduction of hostile operation conditions, cost of the product purification are greatly enhanced. Prasad et al. [68,79,80] have also analyzed the behavior of a circulating fluidized-bed HAMR system utilizing Pd membranes. Their reactor is assumed to operate at steady state by continuously re-circulating the catalyst and adsorbent for regeneration through a second reactor. The ability of Pd membranes to withstand the extreme conditions of the fluidized-bed SRM environment and of the adsorbents to undergo continuous recirculation and regeneration still remain to be validated experimentally. Fayyaz et al. [81] have investigated a detailed model of the HAMR system (shown in Fig. 5) involving a hybrid packed-bed catalytic MR coupling of the SMR through a porous ceramic membrane with a CO_2 adsorption system. The characteristics of HAMR are studied over a range of temperatures and pressures related to the SRM application. It is found that the HAMR system exhibits enhanced methane conversion, hydrogen yield and product purity as compared to conventional MR and SER and shows good promise for reducing the hostile operating conditions of conventional methane-steam reformers for meeting the product purity requirements for PEM operation. Harale et al. [82] have studied the performance of HAMR for the water gas shift (WGS) reaction using layered double hydroxides as adsorbents for CO_2 and nanoporous H_2-selective carbon molecular sieve membranes. The characteristics of the reactor are investigated for a range of temperatures and pressure relevant to the WGS application. The reactor is found to have more potential as compared with the behavior of the traditional packed-bed reactor, the conventional MR and an adsorptive reactor.

3.2. Partial oxidation (PO_x)

The second most common method is partial oxidation in which natural gas or hydrocarbon is heated in the presence of a limited amount of pure oxygen in a reformer; if the amount of oxygen would be more it results in oxidation and a mixture of CO_2 and H_2O will be formed. The hydrocarbons on partial oxidation consist of syngas ($CO+H_2$) and a mixture of carbon dioxide, nitrogen, water vapor and small amounts of by-products, such as methane. CO on WGS reaction gives the final product of H_2 and CO_2; the remaining CO is reduced to trace levels by preferential oxidation to carbon dioxide over a suitable catalyst. This is an exothermic reaction (Eqs. (6) and (7)) and is considered as a faster reaction than steam reforming [83].

$$C_nH_m+(n/2)O_2\rightarrow nCO+(m/2)H_2 \quad (6)$$

$$CO+H_2O\rightarrow CO_2+H_2 \text{ (small amt. of heat)} \quad (7)$$

This method is an expensive method as it requires pure oxygen and the cost is compensated to some extent by the evolution of a large amount of heat which is recovered in downstream. PO_x shows several advantages when compared to other reforming technologies like good response time, compactness, and less sensitivity to the fuel variation. Consequently, small-scale PO_x systems are receiving much interest in the energy utilization field in both stationary and mobile applications [84]. The schematic flow diagram of the process of PO_x is shown in Fig. 6 [83]. However, based on the method of hydrogen production, the partial oxidation is further divided into (i) thermal partial oxidation and (ii) catalytic partial oxidation.

3.2.1. Thermal partial oxidation (TPO_x)

The thermal PO_x is non-catalytic PO_x and requires a high temperature of 1150–1315 °C [83]. It is characterized by the ability to operate with a range of feedstock like methane to heavy fuel oil. The feedstock flexibility according to price and availability is the major attraction of TPO_x and heavy fuel oils are used for their low cost availability [85]. The two commercially important non-catalytic processes are the Texaco process [86,87] and the Shell

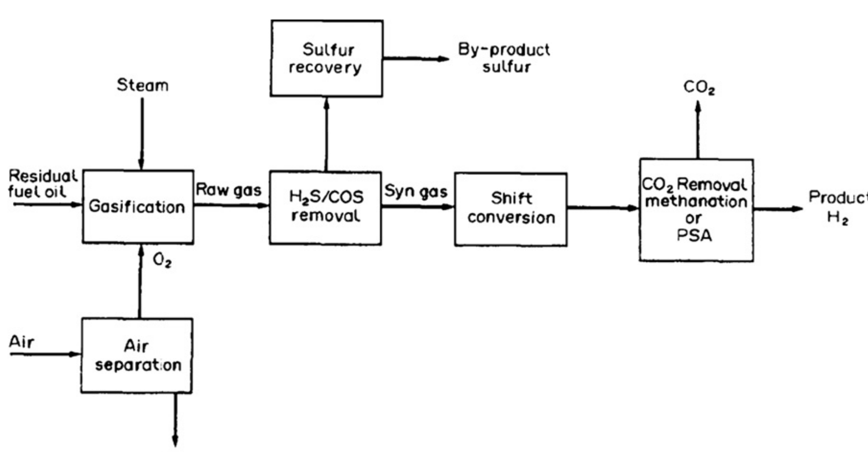


Fig. 6. Simplified flow diagram of hydrogen production from residual fuel oil partial oxidation (PO_x) [83].

process [88,89]. As TPO_x is a very high temperature process, effective catalysts are used to bring down the temperature for oxidation which is dealt with in Section 3.2.2.

3.2.2. Catalytic partial oxidation (CPO_x)

Since SMR is an extremely endothermic process, which leads to many engineering problems like thermal resistance and mechanical strength of the materials used, catalytic partial oxidation is used to overcome these problems. CPO_x is an attractive alternative to the well established SMR process. Furthermore, compared to PO_x, it is operated at lower temperatures and the possibility of soot formation is also lower. Thermodynamically, partial oxidation is a mild exothermic reaction and has a high reaction rate. Use of catalyst reduces the reaction temperature up to 590 °C in CPO_x. Catalysts being non-resistant to sulfur (sulfur < 50 ppm), low sulfur fuel is required and more attention is given for preparation of effective catalysts to make CPO_x more competitive [83].

Paturzo et al. [90] have performed several experiments using different catalysts and reaction conditions in order to achieve the best method for partial oxidation. They have conducted the conversion of methane into syngas in a catalytic membrane reactor containing one- and two-layer Ru membranes. The catalytic membrane consists of a commercial ceramic tube, where two different layers of ruthenium nanoparticles are deposited on the inner surface. Ru is deposited by decomposition of Ru complex in hydrogen stream under mild conditions. The consecutive Ru deposition inside a commercial ceramic support affects methane conversion at each temperature investigated. The maximum methane conversion is achieved at about 59% at 500 °C for a certain membrane reactor configuration. Membrane reactors equipped with a catalytic membrane may be used for their easier and cheaper preparation. Although the H_2/N_2 selectivity seems low (2.3–2.8), particular benefits toward methane conversion are also due to the fine catalyst distribution, as well as good catalyst activity over a ceramic commercial tubular support. This study shows that Ru deposited catalytic membrane gives methane conversion values near the thermodynamic predictions, at each temperature investigated.

A nickel-based catalytic reformation study has been performed [91] using hydrotalcite precursors and promoted with lanthanum and cerium for hydrogen production with simulated hot coke oven gas (COG) and toluene as a model tar compound. A H_2 yield of 86.8% and a CO yield of 87.2% have been achieved at 875 °C. The increase of toluene content in feed gas and reaction temperature is beneficial to improve the oxygen permeation flux. The addition of promoters benefits the performance of catalysts by increasing the oxygen permeation flux and decreasing the carbon formation, which shows a potential application for hydrogen production from hot COG by catalytic partial oxidation reforming of hydrocarbons in the membrane reactor.

Zhan et al. [92] have performed the experiment over perovskite solid oxide fuel cell using dual phase composite membrane reactor. They have shown that catalytic activity depends upon the reaction temperature and CH_4 feedstock or O_2/CH_4 ratio and under the optimized membrane reactor conditions, 88% CO and 89% H_2 selectivity at 30% CH_4 conversion is achieved. The results show that the decreasing O_2/CH_4 ratio favors the increasing CO and H_2 selectivity and the reactivity for partial oxidation of methane is enhanced greatly in the membrane reactor as compared to fixed-bed reactor because of their different manners of oxygen supplying.

3.3. Auto-thermal reforming (ATR)

Auto-thermal reforming is a combination of steam reforming with partial oxidation process in a single reactor. Natural gas is first oxidized into syngas ($CO+H_2$) in a catalytic furnace and then CO reacts in the presence of water to form CO_2 and H_2 by a catalytic shift reaction. CO_2 formed at the end is captured by amines through an absorption process. Presently Aqueous Amine Solvent is the only technique used at industrial scale for the absorption of CO_2 [93]. This method does not require external heat supply because the exothermic heat produced by PO_x directly fulfills the demand of SMR. It consists of a thermal zone in which the temperature rises due to exothermic PO_x and decreases due to endothermic SMR. An important advantage is that it can be stopped and started rapidly while producing a larger amount of hydrogen. To run the ATR reaction properly, the ratio of O_2: fuel and steam: C should be controlled at all times in order to control the reaction temperature and product gas composition while preventing by-products [94–96]. This method has been used for decades and was mainly used in the 1950s and 1960s for the synthesis of syngas for ammonia and methanol production.

Catalysts play an important role in the ATR process and though various kinds of catalysts have been considered nickel is widely used because of its low cost and excellent C–C bond cleavage activity [97,98]. The performance of nickel catalyst in ATR depends upon the nature of supporting material as the supporting element affects the dispersion and stability of the catalyst [99]. Youn et al. [99] have used different supports like ZnO, MgO, ZrO_2, TiO_2 and Al_2O_3 to prepare nickel catalyst by the impregnation method and applied them for hydrogen production from ethanol. Among these supported catalysts, it is found that the catalytic performance of ZrO_2 and TiO_2 supported catalysts is better than that of the other supported catalysts because the electronic structure of nickel species supported on ZrO_2 and TiO_2 is favorably modified which increases the reducibility of nickel species due to the weak interaction between nickel and the support. However, the Ni supported on MgO and ZnO exhibits poor catalytic performance in the ATR of ethanol, because the solid solution phase prevents the formation of an active metallic nickel. The acidity of supported nickel catalysts plays an important role in determining the catalytic performance. It is revealed that the Ni/ZrO_2 and Ni/TiO_2 catalysts with moderate acidity exhibit high catalytic performance.

Several extensive studies have been carried out on noble metal catalysts to achieve high yield of hydrogen at low temperature, but the high cost of noble metals is the main constraint for the successful application of this technology [100]. It has been reported that non-noble metal based catalysts also exhibit relatively high catalytic performance in the auto-thermal reforming of ethanol [22,101].

Youn et al. [97] have also performed experiments for testing the effect of the addition of second metal to nickel catalyst supported on γ-Al_2O_3 on the catalytic performance in ATR of ethanol. Among the tested metals like Ce, Co, Cu, Mg and Zn, Cu is found to be the most efficient promoter for hydrogen production. They have established that Cu species are active in water gas shift reaction for hydrogen production from syngas and that it serves as a barrier for preventing the Ni particles growth. Particularly, the addition of Cu decreases the interaction between Ni species and γ-Al_2O_3 which leads to the facile reduction of Ni-Cu/γ-Al_2O_3 catalyst. Among the 20NixCu (x=3, 5 and 7) catalysts, the 20Ni5Cu catalyst that retains an intermediate state of Cu species between copper aluminate and copper oxide shows the best performance in the auto-thermal reforming of ethanol. Later on Youn et al. have investigated the performance of nickel catalyst supported on different modified zirconia supports. The different amount of the modifying agents which gives the best performance for ATR of ethanol is presented in Table 4. The improved performance observed in the modified support may be attributed to the enhancement of oxygen vacancy and reducibility of nickel on the supports. A comparison between SMR, PO_x and ATR is presented in Table 5 [30,107,108].

Table 4
Performance of Ni catalyst supported on different zirconia supports in the ATR of ethanol.

Sl. no.	Support	Nickel loading	Best composition	References
1	Ce-modified mesoporous zirconia ,Ce/Zr molar ratio X (X=0, 0.1, 0.3, 0.5, 0.7, and 0.9)	20%	Ni/Zr–Ce-0.7	[102]
2	$Ni_5Ti_xZr_{5-x}O_{15}$ (x=0, 1, 2.5, 4, and 5)		$Ni_5Ti_1Zr_4O_{15}$	[103]
3	Mesoporous yttria-stabilized zirconia , Y/Zr molar ratio X (X=0, 0.1, 0.2, and 0.3)	20%	Ni/YSZ-0.1	[104]
4	Mesoporous zirconia supports ($M–ZrO_2$) (M=Zr, Y, La, Ca, and Mg)	20%	$Ni/Y–ZrO_2$	[105]
5	($Ti_XZr_{1-X}O_2$) with different Ti content (X)		$Ni/Ti_{0.2}Zr_{0.8}O_2$	[106]

Table 5
Comparison between reforming processes [30,107,108].

Technology	Advantages	Disadvantages
SMR	• O_2 not required • Lowest temp. • Best H_2/CO ratio • High efficiency • Cost for large unit • Mostly used process	• Highest CO_2 emission • System is complex • System is sensitive to Natural Gas Qualities
PO_x	• No catalyst required • Low methane slip • Simple system • Cost for small unit • Requires less desulphurization	• Low H_2/CO ratio • Very high temp • Soot formation/handling adds complexity • Pure O_2 requires
ATR	• Lower process temperature than PO_x • Low methane slip • Requires less O_2 than PO_x	• Limited commercial experience • Requires air or oxygen

3.4. Steam-iron process

Steam-iron process is considered as the one of the oldest methods and has been used in the early 1900s for the commercial production of hydrogen; the temperature requirement is relatively high, i.e. in the range of 750–850 °C [109]. The benefit of the steam-iron process compared to other thermochemical routes of biomass is that pure hydrogen can be produced in a two-step redox cycle, without the need of any purification steps (like HT-shift, LT-shift and PSA) and has an application in fuel cells [110,111].

Steam iron is a cyclic process for water cleavage, whereby coal, oil and biomass are consumed. The process comprises two steps; the first step is reduction in which the feedstock is gasified to a lean reducing gas, containing carbon monoxide and hydrogen. This reducing gas reacts with iron oxides (hematite: Fe_2O_3, magnetite: Fe_3O_4, wuestite: FeO) to produce a reduced form of iron oxide (FeO) and/or metallic iron. Furthermore, unreacted hydrocarbon, CO and H_2 can be expected and can be reused in the reduction or used for energy supply in the process. Recycling of the spent reducing gas will only be effective when reduction products (CO_2 or H_2O) can be separated or when by-products, such as hydrocarbons, are converted in a recycler by reforming to H_2 and CO. The second step is the oxidation step, where hydrogen is produced as a result of the reaction of steam with the reduced iron oxide [112]. The temperature decreases during reduction whereas during the oxidation, the temperature increases. The energy produced in the exothermic oxidation step satisfied the part of energy required for the gasification/reduction reactor [113]. The hydrogen produced will be sufficiently pure (99.9 vol%). Hydrogen thus obtained can be pure only if the reduced iron oxide is not contaminated with carbon-containing compounds. The advantage of this process is that the hydrogen production is performed separately from the feedstock gasification. Therefore, removal of contaminants, such as tar, CH_4, CO and CO_2, is minimal compared to other proposed biomass-to-hydrogen routes [114]. Through this process, hydrogen can be produced as and when required.

Redox reactions steps are summarized as follows:

Reduction:

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O \quad (8)$$

$$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2 \quad (9)$$

$$Fe_3O_4 + CO + 3H_2 \rightarrow 3Fe + CO_2 + 3H_2O \quad (10)$$

$$Fe_3O_4 + 4CH_4 \rightarrow 3Fe + 4CO + 8H_2 \quad (11)$$

Oxidation:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \quad (12)$$

Otsuka et al. [110,115,116] have proposed the use of reversibly redox system for storing and supplying hydrogen to fuel cell based on the reduction of iron oxide by hydrogen. The metallic iron produced can be easily stored and when necessary, the iron can be reoxidized by water, producing pure hydrogen. When H_2 is needed, Fe^0 reacts with H_2O to produce CO-free hydrogen and the iron oxide is reduced again to Fe^0 making this system cyclic [117]. Gasification of coal and biomass and pyrolysis of oil can be coupled with steam-iron process for the production of hydrogen. Iron oxide can be used in the process as it is a cheap and abundant material [112]. A block diagram of this process is shown in Fig. 7 [83]. Bleeker et al. [118] have successfully used pyrolysis oil as a reducing agent in the steam-iron process and found that a significant amount of relatively pure hydrogen can be produced in a redox cycle with iron oxides, next to a fuel gas. The use of a catalytic iron oxide resulted in an improved conversion of pyrolysis oil to pure hydrogen, due to the enhanced reforming of hydrocarbons in the reduction step. In the view of upcoming shortage of oil and gas, along with increasing emphasis on

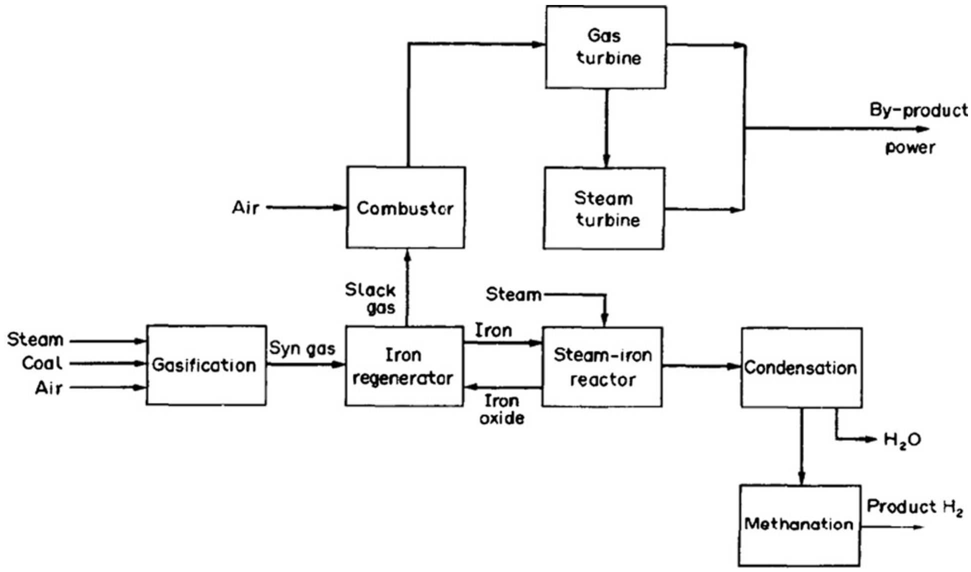


Fig. 7. Simplified flow diagram of hydrogen production from the steam iron process [83].

renewable fuels like biomass, there may be an increased interest in the steam-iron process.

4. Emerging processes for industrial production

In this section, few processes are discussed in which research and development work is in full progress for hydrogen production, though industrial production has not started yet.

4.1. Plasma reforming

Plasma reformation is considered as the latest method for the production of hydrogen though this technology is still not used industrially. Plasma is an ionized gas comprised of molecules, atoms, ions (in their ground or excited states), electrons and photons. It is generated by a method like electrical discharges. It is a highly energetic medium where many chemical reactions are enhanced [119]. The overall reactions are the same as for the conventional reforming and the energy and free radicals are provided by the plasma [120–122]. The reaction is carried out in a reactor called plasmatron; high power plasmatron is a well established technology and is automatic and requires little supervision. Hydrogen-rich gas is produced using air as an oxidizer and has good thermal management in which power consumed in the reaction and the exothermic energy released by PO_x are used to produce the steam required for the system [123]. Since the early 1990s, plasma technologies are gradually attracting attention because of the following reasons:

(i) Compactness and low weight due to high power density.
(ii) Quick response time.
(iii) Fast ignition.
(iv) High conversion efficiencies.
(v) Minimal cost.
(vi) Removal of the catalyst sensitivity to trace impurities in the gas stream.
(vii) Can run with a number of fuels like natural gas, heavy oils and biofuels etc.

It is considered economically attractive [123] for small scale production of hydrogen. The benefit of using this technology is that it makes the path easier by decrementing the cost of

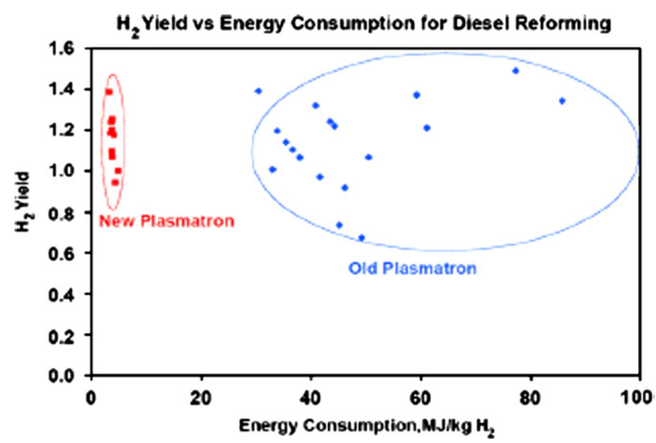


Fig. 8. Comparisons of energy costs for non-thermal and thermal plasmas-reforming of diesel [125].

production, deterioration of catalysts and enhancing the list of feedstock. Another most important advantage over others is that it helps in eliminating CO_2 production by pyrolytic operation, thus providing an option for reducing global warming [124].

Plasma reformation can be categorized as thermal or non-thermal plasma; the difference between these two kinds is the temperature of the ionized gas and the energy of electrons generated during ionization. The products formed are similar but energy consumption in thermal plasma reformation is much higher since most of the energy is used to heat up the particles. The basics of these two kinds of plasma are available in Refs. [120–122]. Bromberg et al. [125] have shown that comparable H_2 yields can be attained with both kinds of plasma, but at significantly lower energy consumption in the case of non-thermal plasma (Fig. 8): “new plasmatron” and “old plasmatron” refer to non-thermal and thermal plasma assisted reformers, respectively. The recent development in this field is the combination of plasma and catalysis under moderate temperatures. The plasma catalysis techniques are divided into categories i.e. single stage system and two-stage system depending on the position of the catalyst. In the single stage plasma type, catalysts are coated on the surface of electrodes or catalyst pellets are constructed within the plasma zone. They are in direct contact with each other so that they can interact directly. In two-stage systems, the plasma zone is placed

either upstream (called preprocessing) or downstream (called post-processing) of the catalyst bed. In plasma preprocessing, plasma either converts reactants into more reactive species or it provides reactive species itself; this method is mostly adopted for the two-stage system while in case of post-processing, plasma vanishes the undesired by-products and converts the residual reactants generated by thermal catalysis [126].

Several researchers are working in this field [122,127,128]; the detailed review of the plasma reformation technique is beyond the scope of this review, but a comprehensive review is presented by Petitpas et al. [129].

4.2. Photoelectrochemical (PEC)

In the PEC process, solar energy is converted into chemical energy in the form of hydrogen through photoelectrolysis. Water is split into hydrogen and oxygen using semiconductors and sunlight [130]. Different semiconductors work at particular wavelengths of light and energies. PEC is considered to be one of the most promising technologies for hydrogen production as it is based on perpetual solar energy, is environmentally safe and can be used on both large as well as small scales and the technology is uncomplicated [131]. In 1972, Fujishima and Honda first discovered this process by using n-type TiO_2 as the anode to cleave water into H_2 and O_2 [132]. Since then, a number of photoelectrodes have been investigated such as WO_3, Fe_2O_3, TiO_2, n-GaAs, n-GaN, CdS, and ZnS for the photoanode; and Cu(In,Ga)Se2/Pt, p-InP/Pt, and p-SiC/Pt for the photocathodes [133–136]. Titanium dioxide (TiO_2) has been proven to be one of the most effective materials because of its attractive photocatalytic activity, photostability and other advantages such as nontoxicity and low cost [137,138]. Zhou et al. [139] have prepared nanostructured carbon-doped thin film TiO_2 (C-TiO_2) by pulsed laser deposition on indium-doped tin oxide (ITO) substrate and have analyzed X-ray diffraction and X-ray photoelectron spectroscopy and have estimated PEC property by evaluating the hydrogen generation efficiency by water splitting in a two compartment electrochemical system. It is observed that the rate of gas production is fastest when the thin film is irradiated by light at a wavelength of 325 nm. On application of a bias potential across photoelectrodes, the hydrogen production is effectively enhanced and addition of organic substance degrades the photoanodic chamber which has resulted in the enhancement of hydrogen generation. Zhang et al. [140] have reported that the improvement of hydrogen production efficiency in PEC water splitting occurs on the fabricated lotus-root-shaped, highly smooth TiO_2 nanotube (TiO_2 NTs) arrays which are prepared by a two-step anodization method. The TiO_2 NTs prepared in the two-step anodization process show better surface smoothness and tube orderliness than TiO_2 NTs prepared in the one-step anodization process. The photon-to-hydrogen conversion efficiency is found to be increased from 0.18% (1-step TiO_2 NTs) to 0.49% (2-step TiO_2 NTs). It is suggested that TiO_2 NTs play an important role in improving the PEC water splitting application for hydrogen generation.

4.3. Thermochemical water splitting process

Present day research is oriented on three major ways of producing hydrogen from water. These are pure thermochemical methods, pure electrolysis methods and hybrid methods. The thermochemical water splitting processes promise to produce hydrogen and oxygen from water and heat without using electricity. This process is also called high temperature water splitting process, where the chemical reactions are driven by high temperature heat in the range of 500–2000 °C [141]. In the 1960s, Funk and Reinstorm [142] made several investigations for hydrogen production from water splitting and evaluated the energy requirements and the possibility of employing two-step processes for water dissociation and hydrogen production by oxides and hydrides. Researchers have identified cycles appropriate to specific temperature ranges and are examining these systems in the laboratory [141]. The research collaboration of General Atomics (GA), Sandia National Laboratory (SNL) and University of Kentucky (UK) found 115 unique thermochemical cycles out of which only 25 cycles are selected for screening and evaluation [143]. Two important cycles namely sulfur–iodine cycle and solar concentration cycle are considered as the most promising processes for the conversion of water into hydrogen and oxygen. These two cycles are described briefly in the following paragraphs.

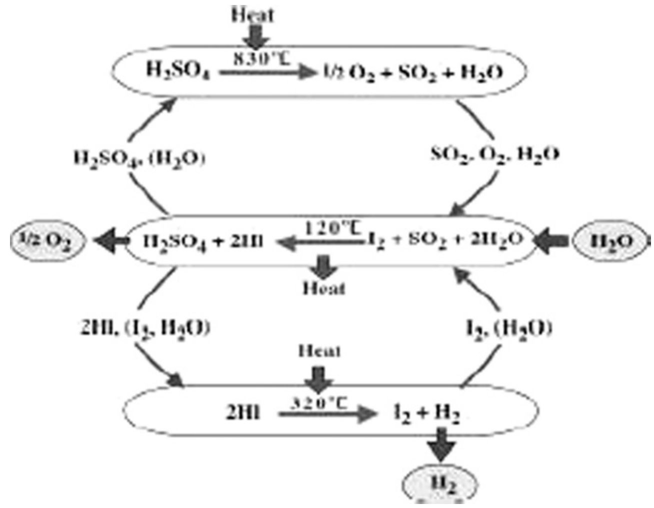


Fig. 9. The sulfur–iodine cycle [144].

4.3.1. Sulfur–iodine cycle

The sulfur–iodine water splitting reaction consists of three steps; the first step is called the Bunsen reaction, the second is the decomposition of sulfuric acid and the third step is the acid HI decomposition step [144]. The cycle operates in the temperature range of 25–927 °C [145]. The chemical reactions are given in Eqs. (13)–(15). The sulfur–iodine cycle is shown in Fig. 9 [144].

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4 \tag{13}$$

$$H_2SO_4 \rightarrow SO_2 + 2H_2O + 0.5O_2 \tag{14}$$

$$2HI \rightarrow I_2 + H_2 \tag{15}$$

All the chemicals are completely recycled, creating a closed loop that consumes only water and produces hydrogen and oxygen. Among the large scale, cost effective and environmentally attractive hydrogen production processes, the sulfur–iodine (S–I or I–S) cycle is quite a promising one. The S–I cycle does require high temperatures, but offers the prospects for high efficiency conversion of heat energy to hydrogen energy. One of the major advantages of using the S–I cycle is that this process is virtually free from harmful by-products and the emission of gases. If it can be heated with a nuclear source, it can prove to be an ideal environmental solution for hydrogen production. Another more important advantage is that it offers higher efficiency than any other hydrogen production processes [146]. The efficiency of the sulfur–iodine process is directly dependent on temperature (Fig. 10) [147]. As the S–I cycle is widely used around the world today, more research is going on about this topic. They try to decrease the heat energy used in the cycle and to make the

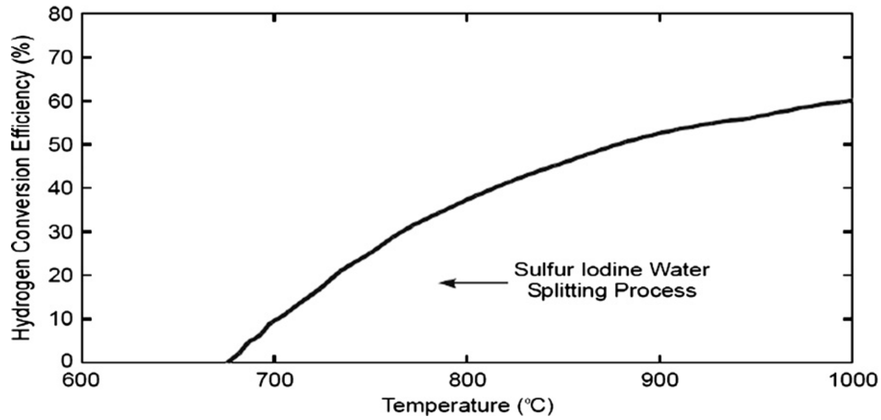


Fig. 10. Efficiency of the sulfur–iodine process vs temperature [147].

process more efficient [148]. Zhang et al. [149] have tested Pt/CeO_2 catalysts with different calcination temperatures to evaluate their effect on hydrogen iodide (HI) decomposition in the sulfur–iodine cycle at various temperatures. It is found that the Pt/CeO_2 catalysts strongly enhance the decomposition of HI to H_2 by comparison with blank yield, especially the catalysts calcined at high temperature. Platinum is introduced into ceria to form the Pt/CeO_2 catalysts by sol–gel. It is found that, through the sol–gel method, the Pt ions could be inserted into the ceria lattice. This brought about a different synergistic effect between the Pt and Ce components, such as increase of the oxygen mobility in ceria support and improvement of the thermal stability of catalyst, and it is found as a potential material used in the sulfur–iodine cycle for hydrogen production. They [150] have also investigated the effect of oxidation/reduction processes on the activity of catalyst Pt/CeO_2; it is observed that the encapsulation of Pt by ceria support affected the activity of the catalyst and at temperature below 400 °C, the reduced sample exhibits the best activity. Furthermore, Zhang et al. [151] have evaluated the effect of $Pt/Ce_{1-x}Zr_xO_2$ catalysts with different Zr concentrations (where $x=0$, 0.2, 0.5, 0.8, 1) on HI decomposition at various temperatures. It is found that on introduction of ZrO_2 into Pt/CeO_2, the synergistic effect between Pt and CeO_2–ZrO_2 solid solution is different from Pt and CeO_2 yield with respect to improvement of the thermal stability and increase of Pt–O–Ce reducibility. Among the three samples containing Zr, the one with 20 mol% displays the best activity for hydrogen production. Zhang et al. [152] have performed a number of experiments to observe the catalytic properties of nickel supported on ceria prepared by different methods and have found that pure ceria strongly enhances the decomposition of HI to hydrogen as compared to the blank yield. The Ni/CeO_2 catalyst shows better catalytic activity and it is observed that during the CeO_2 synthesis process of Ni doping, the presence of Ni causes smaller average particle size, larger surface area, better thermal stability and better Ni dispersion than the Ni-loading samples. They [153] have also tested the Ni/CeO_2 catalysts with different calcination temperatures and have performed TG-FTIR, BET, XRD, HRTEM and TPR for catalyst characterization and have found a change in particle size and morphology with the increase in calcination temperature from 300 to 900 °C. The Ni/CeO_2 catalysts show better catalytic activity at the calcination temperature of 700 °C. Later on, they [154] have also shown that the oxidative/reductive atmosphere affects the structure and performance of the Ni/CeO_2 catalysts and it is suggested that during reductive treatment, migration of Ce^{4+} occurs from the bulk to the surface and during oxidative treatment, the diffusion process is reversed. These studies provide nickel–ceria catalyst as a potential material to be used in the SI cycle for HI decomposition.

High-temperature reactors (HTRs) are particularly attractive due to their wide industrial application from electricity generation to hydrogen production. The Japan Atomic Energy Agency's (JAEA's) HTTR (High Temperature Engineering Test Reactor), which is the first HTR in Japan, has attained its maximum reactor-outlet coolant temperature and successfully delivers 950 °C coolant helium outside its reactor vessel. A hydrogen production system based on the thermochemical water-splitting iodine–sulfur (IS) process is planned to be connected to the HTTR in the near future. This will establish the hydrogen production technology with an HTR, including the system integration technology for connection of hydrogen production system to HTRs. It will probably be the world's first demonstration of hydrogen production directly using heat supplied from an HTR. It is expected that the HTTR-IS system will be the world's first water-splitting hydrogen production demonstration by using the direct heat from a high-temperature gas-cooled reactor and the verification of the hydrogen production by a nuclear system is greatly expected to produce a massive quantity of hydrogen in coming hydrogen society [155].

4.3.2. Solar concentration cycle

In this method, a solar concentrator is used which consists of mirrors and a reflective or refractive lens to capture and focus sunlight to produce temperatures up to 2000 °C. This high-temperature heat can be used to drive chemical reactions that produce hydrogen. This process is carried out via two steps. The first step is an endothermic step in which metal oxide powder passes through the reactor which is heated by a solar concentrator and operating at a high temperature. At this temperature metal oxide is dissociated into metal and oxygen gas. In the second step (non-solar exothermic step), the metal reacts with water to form hydrogen gas and metal oxide. The metal oxide formed is again recycled in the first step. The redox reaction of ZnO/Zn based thermochemical cycle is represented by the following equations:

$$ZnO \rightarrow Zn + 0.5O_2 \quad (16)$$

$$Zn + H_2O \rightarrow ZnO + H_2 \quad (17)$$

Since hydrogen and oxygen are formed in different steps, it does not require any separation unit [156]. Several researchers have examined and tested the ZnO/Zn [157–160] and Fe_3O_4/FeO [161–163] and Zn and FeO are found to be important candidates for the solar concentration cycle. Abanades et al. have demonstrated a thermochemical cycle based on CeO_2/Ce_2O_3 [164] oxides in which the first step is performed in an inert atmosphere, and the operating condition is $T=2000$ °C, $P=100$–200 mbar and the second step is carried out in as fixed-bed reactor at a temperature range of 400–600 °C. They have shown cerium oxide as an

important material for pure hydrogen production. Kodama et al. [165] have carried out several studies and have shown that better reactivity and repeatability of the cyclic water splitting are achieved by using ZrO_2-supported $Ni_xFe_{3-x}O_4$, Co(II)–ferrite [166], $NiFe_2O_4$ and Fe_3O_4 powders [167]. Kaneko et al. [168] have developed a new concept for solar hydrogen production and fabricated a new rotary-type solar reactor. They have successfully demonstrated the two-step water splitting process. They have used the reactive ceramics of CeO_2 and Ni–Mn–ferrite ($Ni_{0.5}Mn_{0.5}$-Fe_2O_4) and have observed the evolution of H_2 gas under the applied reaction temperature of the O_2-releasing reaction cell (T: 1350 °C) and H_2-generation reaction cell (T: 1000 °C). The repetition of the two-step water-splitting process is achieved by using the reactive ceramics of Ni–Mn–ferrite and the optimum reaction temperatures of the O_2-releasing and H_2-generation reactions are 1200 °C and 900 °C respectively. The rotary-type solar reactor concept is studied in laboratory scale and seems to be one of the most promising thermochemical energy conversion devices to produce solar hydrogen.

4.3.3. Hybrid sulfur process

This thermochemical process is a combined cycle process of thermochemical and electrolytic reactions of water splitting. This process runs at a low temperature using electricity [169] and is also known as the Ispra Mark 11 Cycle and Westinghouse cycle. This process has the same high-temperature endothermic reaction as the S–I cycle. The hybrid sulfur process consists of two steps:

$$H_2SO_4 \leftrightarrow SO_2 + H_2O + 1/2O_2 \text{(Thermochemical, 800–900 °C)} \quad (18)$$

$$2H_2O + SO_2 \leftrightarrow H_2SO_4 + H_2 \text{(Electrochemical, 100–120 °C)} \quad (19)$$

A schematic block diagram of hybrid sulfur process is shown in Fig. 11. This process can be thought of as consisting of three different sections. The first section includes the electrolyzers and their associated equipment. Next are the sulfuric acid concentration and decomposition operations, which produce water and gaseous mixtures of SO_2 and oxygen. Finally, the need to separate a clean O_2 product stream from the SO_2/O_2 mixture coming from sulfuric acid decomposition and dissolve the remaining SO_2 in the anolyte leads to a third flow sheet section where these tasks are accomplished. The overall net thermal efficiency for the hybrid sulfur cycle is calculated to be 48.8% [170]. The energy efficiency

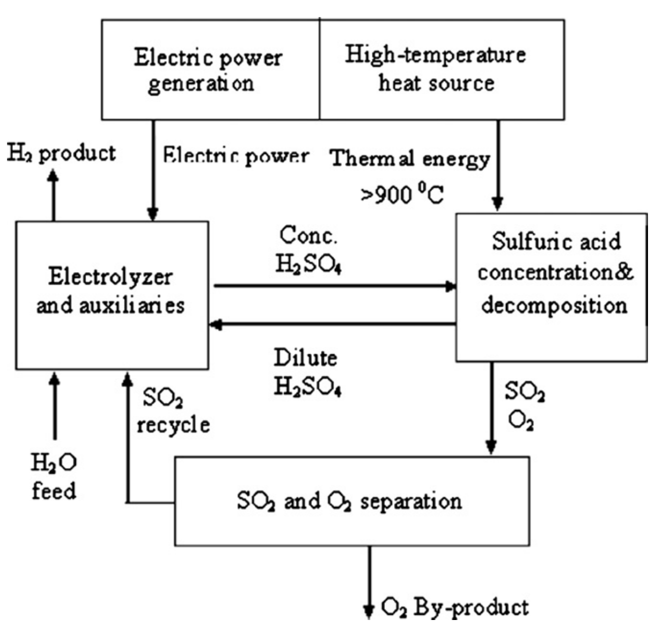


Fig. 11. Schematic block diagram of hybrid sulfur [170].

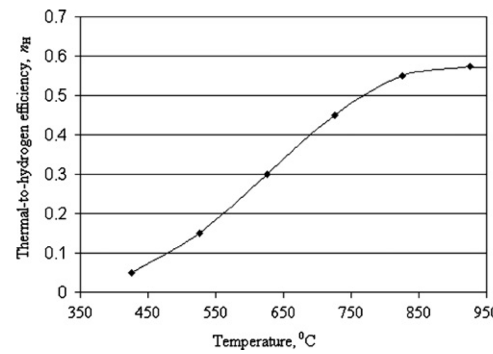


Fig. 12. Thermal-to-hydrogen energy efficiency for Westinghouse sulfur process coupled to a GT-MHR [169].

based on the thermal and electrical energy use from a gas turbine modular helium reactor (GT-MHR) is shown in Fig. 12 [169]. Jeong [171] has estimated the efficiency of the hybrid sulfur cycle under a variety of operating conditions by using softwares CHEMKIN [172] and CANARY [173] and has found a maximum efficiency of 47% under the condition of 10 bar and 927 °C for the decomposer.

Among all the thermochemical water splitting cycles, sulfur based cycles like sulfur–iodine and Westinghouse cycle have been gaining more interest over the decades. In these processes, platinum supported on titania has been identified as a highly active sulfuric acid decomposition catalyst [174] and the deactivation of catalyst is a major problem [175]. Ginosar et al. [176] have been performing experiments by adding higher melting point platinum group metals to improve catalyst stability. They have found that when either Ru, Rh, or Ir is added to the 1% Pt–TiO_2 catalyst, deactivation rates decreased by a factor of three and reaction rates at the end of one week testing are improved by up to four fold.

Kodama et al. [177] have examined the thermochemical two-step water splitting on ZrO_2-supported Co(II)–ferrites below 1400 °C, for the conversion of solar high-temperature heat into clean hydrogen energy. They have thermally decomposed the ferrite supported on ZrO_2 to the reduced phase of wustite at 1400 °C under an inert atmosphere. Then the reduced phase is reoxidized with steam on the ZrO_2-support to generate hydrogen below 1000 °C in a separate step. Kodama et al. [178] also have examined redox metal for Ni(II) ferrites or $Ni_xFe_{3-x}O_4$ ($0 \le x \le 1$) for converting solar high-temperature heat to hydrogen. In this experiment the Ni(II) ferrite is decomposed to Ni-doped wustite ($Ni_yFe_{1-y}O$) at 1400 °C under an inert atmosphere in the first thermal-reduction step of the cycle; it is then reoxidized with steam to generate hydrogen at 1000 °C in the second water-decomposition step.

4.4. Biological process

The important advantage of biological process is the use of renewable energy resources at ambient pressure and temperature over chemical methods [179]. Since the eighties, this process has been gaining interest and a huge number of research papers have been published in various reputed journals. In the early days, only glucose was used as the feedstock but now attention is given to starch, sucrose, cellulose and waste materials. This process can be mainly divided into four categories as given below.

(i) Biophotolysis of water using green algae and blue-green algae (cyanobacteria).
(ii) Photo-fermentation.
(iii) Dark fermentation.
(iv) Hybrid systems.

Among these processes, dark fermentation and photo-fermentation are considered as the promising processes [180,181]. These processes are briefly described below.

4.4.1. Biophotolysis

It is comprised of direct biophotolysis and indirect biophotolysis.

4.4.1.1. Direct biophotolysis. This process involves photosynthetic reaction where solar energy is converted into chemical energy by using microalgae (green algae and Cyanobacteria). The chemical reaction is written as follows:

$$2H_2O+\text{Solar Energy}\rightarrow 2H_2+O_2 \tag{20}$$

During photosynthesis, algae splits water molecules into hydrogen and oxygen ions and the enzyme hydrogenase converts hydrogen ion into hydrogen gas. During the process, the light energy is absorbed by the pigments at photosystem I (PSI), photosystem II (PSII) or both, which raises the energy level of electrons from water oxidation when they are transferred from PSI via PSII to ferredoxin (Fd) [182]. The hydrogenase accepts the electrons from Fd to produce hydrogen as shown in Fig. 13 [183].

Anabaena cylindrica is the most common cyanobacteria for direct biophotolysis. In recent years, *A. variabilis* has gained more attention because of its higher hydrogen producing capacity [184–188]. Direct biophotolysis process seems to be very attractive as it uses water and solar energy for hydrogen production and theoretical efficiency of solar energy conversion can be more than 80% [189,190] but in actuality, efficiency is very low due to genetic tendency of green algae to assemble in a large array of light absorbing chlorophyll antenna in their photo-systems [191–194].

4.4.1.2. Indirect biophotolysis. It consists of two steps where the first step is comprised of photosynthesis which gives rise to glucose and in the second step, glucose and water give H_2 and CO_2 by light-induced process. The photo-chemical reactions are described as follows:

$$6H_2O+6CO_2+\text{light energy}\rightarrow(C_6H_{12}O_6)_n+6O_2 \tag{21}$$

$$(C_6H_{12}O_6)_n+12H_2O+\text{light energy}\rightarrow 12H_2+6CO_2 \tag{22}$$

A number of green algae and cyanobacteria can fix nitrogen from the atmosphere and produce enzymes which catalyze the second H_2 generating step. Cyanobacteria are the ideal candidates for this process as they have the simplest nutritional requirement [180,181]. Maximum light conversion efficiency is 16.3% [195] but with increasing light illumination, conversion efficiency decreases. In actuality practice efficiency is only 1–2% [196–200]. Nonutilization of waste and low hydrogen production potential by algae are the two disadvantages of this process [16].

4.4.2. Photo-fermentation

Photosynthetic bacteria like *Rhodobacter spheroides* [200–202], *Rhodobacter capsulatus* [203,204], *Rhodovulum sulfidophilum W-1S* [205] and *Rhodopseudomonas palustris* [206] produce hydrogen in the presence of nitrogenase enzyme by using light energy and organic acids (e.g. acetate, lactate, butyrate, maltate etc.) or biomass in open ponds or photobioreactors [207]. The overall reaction is given as follows:

$$C_6H_{12}O_6+12H_2O\overset{\text{Light Energy}}{\rightarrow}12H_2+6CO_2 \tag{23}$$

Recently, some attempts have been made to effect waste management by utilizing biomass wastes for hydrogen production. Ni et al. [183] have compared the hydrogen conversion efficiency from different biomass wastes which is described in Table 6.

Photo-fermentation process takes place in oxygen deficient conditions and limited amount of ammonia as the presence of oxygen or ammonia inhibited the nitrogenase enzyme [209]. This process has the following disadvantages:

(i) The nitrogenase enzyme has high-energy demand.
(ii) Solar energy conversion efficiencies are low.
(iii) It requires elaborate anaerobic photobioreactors covering large areas [202,207].

One of the major problems for hydrogen production from industrial effluents is the color of the wastewater, which can reduce the penetration of light and the high concentration of ammonia reduces the hydrogen productivity. The presence of some toxic compounds in industrial effluents will require pre-treatment before using them for hydrogen gas production [16]. The yield of 80% has been achieved in this process. The flow diagram of photo-fermentation is shown in Fig. 14 [210]. Due to its several drawbacks like the (i) use of nitrogenase enzyme with

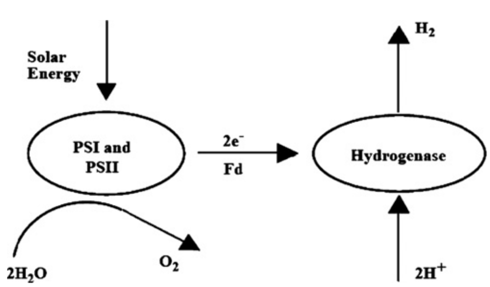


Fig. 13. Schematics of direct biophotolysis [183].

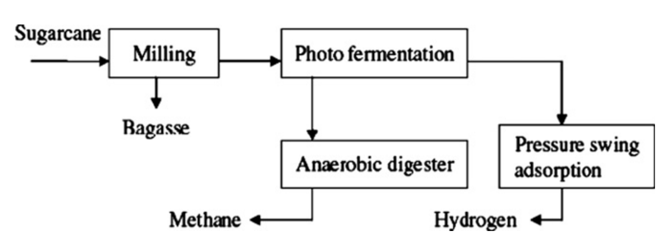


Fig. 14. Flow diagram of photo-fermentation process [210].

Table 6
Studies on hydrogen production by photo-fermentation (adapted from [183]).

Biomass Type	Bacteria system	Hydrogen conversion efficiency	References
Lactic acid	*Rhodobacter sphaeroides* immobilized	86%	[131]
Lactate feedstock	*Rhodobacter capsulatus*	30%	[138]
Wastewater	*Rhodobacter sphaeroides* immobilized	53%	[139]
Sugar refinery wastewater	*Rhodobacter spaeroides* O.U.001	0.005 l H_2/h/l culture	[140]

high-energy demand, (ii) low solar energy conversion efficiency and (iii) demand for elaborate anaerobic photobioreactors covering large areas, this process is not regarded as a very competitive method for hydrogen production [202].

4.4.3. Dark fermentation

The fermentation is carried out in the dark by anaerobic bacteria and some microalgae like green algae on carbohydrate-rich substrate [211]. This reaction can be operated at mesophilic, thermophilic, extreme thermophilic or hyperthermophilic temperatures [212]. The products of this process are mostly H_2 and CO_2 combined with other gases like CH_4 or H_2S, depending on the reaction process and the type of substrate used. When glucose is used as a substrate, 4 mol of H_2 is produced per mol of glucose and the end product is acetic acid and when the end product is butyrate, 2 mol of H_2 is produced per mol of glucose. But in actual practice, the end product contains both acetate and butyrate and 4 mol H_2 per mol of glucose cannot be achieved [213]. The process is described in Fig. 15 [183]. The hydrogen production yield depends upon the *pH* value, hydraulic retention time (HRT) and gas partial pressure. The *pH* should be maintained between the values of 5–6 for the maximum yield of hydrogen. As this process does not require light energy, not much land is required and it is unaffected by the weather conditions. The feasibility and success of this technology will yield a growing commercial value in due course of time [183,208].

4.4.4. Hybrid system

This is a new approach in hydrogen production from biological wastes where a combination of dark fermentation and photo-fermentation is used. It is considered as the most promising process because others fail to achieve complete conversion. Tao et al. [214] have demonstrated a two-step process for increasing the hydrogen yield from sucrose. The first step is the dark fermentation using microflora; the maximum hydrogen yield is around 3.67 mol H_2/mol sucrose. The fatty acids produced in the first step are mainly butyrate and acetate with a small amount of propionate, valerate, *n*-butyl alcohol and caproate and in the second step the photo-fermentation process is employed to convert these fatty acids into hydrogen. The hydrogen yield is increased from 3.67 mol H_2/molsucrose to 6.63 mol H_2/mol sucrose in photo-fermentation.

This process has attracted the heed of many scientists and in recent years a number of experiments have taken place. Chen et al. [215] have used the hybrid process and shown the increased hydrogen yield from 3.80 mol H_2/mol (dark fermentation) to 10.02 mol H_2/mol sucrose (dark/photo-fermentation) as well as the 72% reduction of chemical oxygen demand (COD) in the effluent. It is observed that when the photo-bioreactor is illuminated with side-light optical fibers and is supplemented with 2.0% (w/v) of clay carriers, the overall H_2 yield of the two-stage process is further enhanced to 14.2 mol H_2/mol sucrose with a nearly 90% COD removal.

Su et al. [216] have performed a study to investigate this hybrid process from glucose. In dark fermentation, an orthogonal experimental design is used to optimize the culture medium for *C. butyricum* and the maximum hydrogen yield is found to increase from 1.59 to 1.72 mol H_2/mol glucose and the hydrogen production rate is increased from 86.8 to 100 ml H_2/l/h. Then in photo-fermentation, the metabolite by-product, containing acetate and butyrate, is inoculated with *R. palustris* and reutilized to produce hydrogen. The maximum hydrogen yield obtained in photo-fermentation is 4.16 mol H_2/mol glucose, and the maximum removal ratios of acetate and butyrate are 92.3% and 99.8%, respectively. On combining both fermentations, a dramatic increase of hydrogen yield from 1.59 to 5.48 mol H_2/mol glucose is reported. Further they have shown the variation in the improvement of hydrogen yield from various feedstocks like water hyacinth [217], cassava starch [218] and rice straw [219]. Water hyacinth is pretreated with microwave heating and alkali to enhance the enzymatic hydrolysis and hydrogen production in the hybrid system. The pretreated water hyacinth is then used to produce hydrogen by mixed H_2 producing bacteria in dark fermentation, and the maximum hydrogen yield of 76.7 ml H_2/g TVS (total volatile solid) at 20 g/l of water hyacinth is obtained; after that the residual solutions of dark fermentation are used to produce hydrogen in photo-fermentation. The maximum yield of 522.6 ml H_2/g TVS is obtained at 10 g/l of water hyacinth. On combining dark and photo-fermentation, hydrogen yield is enhanced to 596.1 ml H_2/g TVS which is 59.6% of the theoretical

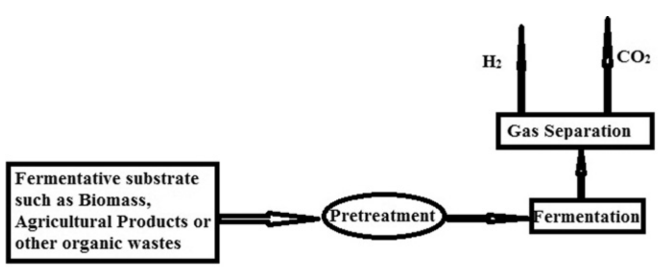


Fig. 15. Hydrogen production by dark fermentation [183].

Table 7
Biological processes with their advantages [221].

Process	Microorganism used	Advantages
Direct biophotolysis	Microalgae	• Solar conversion energy increased by 10-folds as compared to trees, crops
Indirect biophotolysis	Microalgae, Cyanobacteria	• It has the ability to fix N_2 from atmosphere
Photo-fermentation	Microalgae, purple bacteria	• Use different waste materials like distillery effluents, waste etc.
Dark fermentation	Fermentative bacteria	• Use a variety of carbon source as substrate • Can produce hydrogen without light • Produce valuable metabolites as by-products, e.g. butyric acids, lactic and acetic acids • There is no oxygen limitation problem
Hybrid system	Fermentative bacteria + anoxygenic phototropic bacteria	• Can improve the overall yield of hydrogen

hydrogen yield. Su et al. have obtained different hydrogen yields from different concentrations i.e. 10–25 g/l of raw cassava starch in the dark fermentation inoculated with the mixed hydrogen producing bacteria derived from the preheated activated sludge. At a concentration of 10 g/l, a maximum hydrogen yield of 240.4 ml H_2/g starch is obtained and at 25 g/l concentration, the maximum hydrogen production rate was 84.4 ml H_2/l/h. After that, cassava starch gelatinized by heating or hydrolyzed with α-amylase and glucoamylase is used as the substrate to produce hydrogen, the maximum hydrogen yield increases to 258.5 and 276.1 ml H_2/g starch respectively and the maximum hydrogen production rate is found to be increased to 172 and 262.4 ml H_2/l/h. Then the metabolite by-products in the dark fermentation, which are mainly acetate and butyrate, are reutilized as the substrates in the photo-fermentation inoculated with the *Rhodopseudomonas palustris* bacteria. The maximum hydrogen yield and hydrogen production rate are found to be 131.9 ml H_2/g starch and 16.4 ml H_2/l/h respectively in the photo-fermentation. The highest utilization ratios of acetate and butyrate are 89.3% and 98.5% respectively. The maximum hydrogen yield dramatically increases from 240.4 ml H_2/g starch only in the dark fermentation to 402.3 ml H_2/g starch in the combined dark and photo-fermentation, while the energy conversion efficiency increases from 17.5–18.6% to 26.4–27.1% if only the heat value of cassava starch is considered as the input energy. When the input light energy in the photo-fermentation is also taken into account, the whole energy conversion efficiency is 4.46–6.04%. Later Cheng et al. [220] have performed the experiment to improve the hydrogen yield by using mixed anaerobic bacteria and cell immobilization and found the hydrogen yield to be increased from 402 to 840 ml H_2/g starch (from 2.91 to 6.07 mol H_2/mol hexose) in the combination of dark and photo-fermentation. They have also pretreated rice straw by microwave heating for 15 min at 140 °C in 0.5% NaOH solution followed by enzymatic hydrolysis for 96 h. A maximum hydrogen yield of 155 ml/g TVS is obtained when anaerobic bacteria are used to produce hydrogen from hydrolyzed rice straw in dark fermentation. In photo-fermentation, the residual solution from dark fermentation is reutilized by immobilized photosynthetic bacteria. By combining both fermentation processes, the maximum hydrogen yield is found to be greatly enhanced to 463 ml/g TVS which is 43.2% of the theoretical hydrogen yield. Biological processes with their advantages are shown in Table 7 [221].

5. Conclusions

The reforming processes are the mostly used and most efficient method for hydrogen production. SER, MR and HAMR are considered as the recent developments in the SMR process. SER has an advantage of enriched conversion and offers high potential for energy conservation and process simplification. This process allows direct production of high-purity hydrogen (95 mol%) at high methane to hydrogen conversion (80%) at a low temperature of 450 °C and MRs can produce CO-free hydrogen without the complicated H_2 purification units. The MRs are expected to be more energy-effective and compact hydrogen production systems as compared to the conventional systems. A number of research works have been carried out in this field. HAMR is a combination of membrane and adsorption enhanced reactors. It is found to be more advantageous than MRs and SER. A study is performed for CPO_x which results in an 86.8% yield of hydrogen with hydrotalcite promoted with lanthanum and cerium, and 89% H_2 selectivity at 30% CH_4 conversion is achieved with perovskite solid oxide fuel cell using a dual phase composite membrane reactor. Few processes are considered as emerging processes for hydrogen production like plasma reforming, thermochemical water splitting and biological process; though their efficiency is not very high they are gaining interest because of easy availability of feedstock used in these processes. Plasma reformation is the latest method; it makes the path easier by decrementing the cost of production, deterioration of catalysts, enhancing the list of feedstock, and helps in eliminating CO_2 production by pyrolytic operation, providing an option for reducing global warming. The combination of plasma with catalysis is recently developed. In the SI process, high temperature reactors (HTRs) are attractive due to their applications from electricity generation to hydrogen production and it is expected that the HTTR-IS system will be the world's first water-splitting hydrogen production demonstration using the direct heat from a high-temperature gas-cooled reactor and the verification of the hydrogen production by a nuclear system is greatly expected to produce a massive quantity of hydrogen in coming hydrogen society. Biological production of hydrogen provides a viable means for the sustainable supply of hydrogen with low pollution and high efficiency, thereby being considered a promising way of producing hydrogen. A comparative chart is produced in Table 8 for different types of hydrogen production technologies and their efficiencies.

Table 8
Comparison of hydrogen production technologies (adapted from [222]).

Technology	Feedstock	Conversion efficiency	References
SMR	Hydrocarbons	70–85%[a]	[223]
SER	Hydrocarbon	NA	
MR	Hydrocarbon	77–92%	[224]
HAMR	Hydrocarbon	100%	[78]
PO_x	Hydrocarbons	60–75%[a]	[223]
ATR	Hydrocarbons	60–75%[a]	[223]
Steam iron	Hydrocarbons	NA	
Plasma reforming	Hydrocarbons	9–85%[b]	[225]
Photoelectrochemical	Water + sunlight	12.4%[c]	[226]
Hybrid sulfur process	Water + heat	48.8%[d]	[170]
Photolysis	Sunlight + water	1–2%[e]	[196–200]
Photo-fermentation	Organic acids + sunlight	6.6–86%	[16,202,206]
Dark fermentation	Biomass	60–80%[b]	[227]
Hybrid system	Biomass + sunlight	6.04–46%	[216,218,228]

N/A, not available.

[a] Thermal efficiency, based on the higher heating values.
[b] Maximum theoretical yield of 4 moles H_2 per mole glucose catabolized.
[c] Solar to hydrogen via water splitting and does not include hydrogen purification.
[d] Higher heating value (HHV) of the hydrogen product divided by the total thermal energy requirements.
[e] Light conversion efficiency.

Since hydrogen can be produced by diverse renewable sources and helps in minimizing or eliminating global warming, a number of research works have been carried out throughout the world to make hydrogen producing methods more and more efficient. Still the conventional processes for hydrogen production are attractive and economical though non-conventional processes are getting more attention in scientific research. Hydrogen storage is one of the major problems and it needs to be addressed urgently to move to hydrogen fuel utilization. On-board hydrogen production and utilization in automotive vehicles will be a path for moving toward hydrogen fuel. Present authors are working on the production of hydrogen using fossil and renewable sources of hydrocarbon through non-thermal plasma reformation technique. Design and development of a multi-fuel fuel-reformer is the aim of the study which may lead to utilization of the reformer for vehicles. Utilization of renewable sources, solar energy by thermochemical water splitting and biological processes is the ultimate solution for hydrogen production and clean environment.

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